

GAS HYDRATE TUTORIAL

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ABSTRACT

The tutorial provides an overview of time-independent physical/chemical properties as related to crystal structures. Page limitations proscribe only a description of hydrate properties; applications are detailed in other papers in this gas hydrate symposium. The following seven points are illustrated in this tutorial:

1. Gas hydrates are crystalline compounds which form when small ($<0.9\text{nm}$) molecules contact water at temperatures above and below the ice point, with elevated pressures.
2. Properties of sI and sII hydrate crystals are well-defined; measurements have begun on sH.
3. Each volume of hydrate contains as much as 180 volumes (STP) of methane.
4. Physical and chemical properties of hydrates are approximated by three heuristics:
 - Mechanical properties approximate those of ice,
 - Phase equilibrium is set by the size ratio of guest molecules within host cages, and
 - Thermal properties are set by the hydrogen-bonded crystals within a range of guest sizes.
5. Three-phase ($L_w\text{-H-V}$) equilibrium pressure depends exponentially on temperature.
6. There is a need to characterize the hydrate phase directly (via diffraction, NMR, Raman, etc.).
7. No acceptable model exists for hydrate formation kinetics.

The reader may wish to investigate these details further, via references contained in several monographs, (Sloan, 1990; Sloan et al., 1994, Monfort, 1996).

INTRODUCTION

Gas clathrates (commonly called hydrates) are crystalline compounds which occur when water forms a cage-like structure around smaller guest molecules. While they are more commonly called hydrates, a careful distinction should be made between these non-stoichiometric clathrate hydrates of gas and other stoichiometric hydrate compounds which occur for example, when water combines with various salts.

Gas hydrates of current interest are composed of water and the following eight molecules: methane, ethane, propane, isobutane, normal butane, nitrogen, carbon dioxide, and hydrogen sulfide. Yet other apolar components between the sizes of argon (0.35 nm) and ethylcyclohexane (0.9nm) can form hydrates. Hydrate formation is a possibility where water exists in the vicinity of such molecules at temperatures above and below 273 K.

Hydrate discovery is credited in 1810 to Sir Humphrey Davy. Due to their crystalline, non-flowing nature, hydrates became of interest to the hydrocarbon industry in 1934 (Hammerschmidt, 1934), the time of their first observance blocking pipelines. Hydrates act to concentrate hydrocarbons: 1 cubic meter of hydrates may contain as much as 180 SCM of gas. Makogon, (1965) indicated that large natural reserves of hydrocarbons exist in hydrated form, both in deep oceans and in the permafrost. Evaluation of these reserves is highly uncertain, yet even the most conservative estimates concur that there is twice as much energy in hydrated form as in all other hydrocarbon sources combined. While one commercial example exists of gas recovery from hydrates, the problems of *in situ* hydrate dissemination in deepwater/permafrost environments will prevent their cost-effective recovery until the next millennium.

WHAT ARE HYDRATES: HOW DO STRUCTURE RELATE TO PROPERTIES?

Hydrates normally form in one of three repeating crystal structures shown in Figure 1. Structure I (sI), a body-centered cubic structure forms with small natural gas molecules found *in situ* in deep oceans. Structure II (sII), a diamond lattice within a cubic framework, forms when natural gases or oils contain molecules larger than ethane but smaller than pentane. sII represents hydrates which commonly occur in hydrocarbon production and processing conditions, as well as in many cases of gas seeps from faults in ocean environments.

The newest hydrate structure H, named for the hexagonal framework, was discovered and shown by Ripmeester et al. (1987, 1991) to have cavities large enough to contain molecules the size of common components of naphtha and gasoline. Initial physical properties, phase equilibrium data, and models have been advanced (Mehta and Sloan, 1993, 1994a,b, 1996a,b,c; Udachin et al. 1996), and Sassen et al. (1994) have found one instance of *in situ* sH in the Gulf of Mexico. Since information on structure H is in the fledgling stages, most of this tutorial concerns sI and sII.

HYDRATE CRYSTAL STRUCTURES.

Table 1 provides a hydrate structure summary for the three hydrate unit crystals (sI, sII, and sH) shown in Figure 1. The crystals structures are given with reference to the water skeleton, composed of a basic "building block" cavity which has twelve faces with five sides per face, given the abbreviation 5^{12} . By linking the vertices of 5^{12} cavities one obtains sI; linking the faces of 5^{12} cavities results in sII; in sH a layer of linked 5^{12} cavities provide connections.

Interstices between the 5^{12} cavities are larger cavities which contain twelve pentagonal faces and either two, four, or eight hexagonal faces: (denoted as $5^{12}6^2$ in sI, $5^{12}6^4$ in sII, or $5^{12}6^8$ in sH). In addition sH has a cavity with square, pentagonal, and hexagonal faces ($4^35^66^3$). Figure 1 depicts the five cavities of sI, sII, and sH. In Figure 1 a oxygen atom is located at the vertex of each angle in the cavities; the lines represent hydrogen bonds with which one chemically-bonded hydrogen connects to an oxygen on a neighbor water molecule.

Inside each cavity resides a maximum of one of the small, guest molecules, typified by the eight guests associated with 46 water molecules in sI ($2[5^{12}] \cdot 6[5^{12}6^2] \cdot 46\text{H}_2\text{O}$), indicating two guests in the 5^{12} and 6 guests in the $5^{12}6^2$ cavities of sI. Similar formulas for sII and sH are $(16[5^{12}] \cdot 8[5^{12}6^4] \cdot 136\text{H}_2\text{O})$ and $(3[5^{12}] \cdot 2[4^35^66^3] \cdot 1[5^{12}6^8] \cdot 34\text{H}_2\text{O})$ respectively.

Structure I a body-centered cubic structure forms with natural gases containing molecules smaller than propane; consequently sI hydrates are found *in situ* in deep oceans with biogenic gases containing mostly methane, carbon dioxide, and hydrogen sulfide. Structure II a diamond lattice within a cubic framework, forms when natural gases or oils contain molecules larger than ethane but smaller than pentane; sII represents hydrates from thermogenic gases. Finally structure H hydrates must have a small occupant (like methane, nitrogen, or carbon dioxide) for the 5^{12} and $4^35^66^3$ cages but the molecules in the $5^{12}6^8$ cage can be as large as 0.9nm (e.g. ethylcyclohexane).

TIME-INDEPENDENT PROPERTIES FROM HYDRATE CRYSTAL STRUCTURES.

Mechanical Properties of Hydrates. As may be calculated via Table 1, if all the cages of each structure are filled, all three hydrates have the amazing property of being approximately 85% (mol) water and 15% gas. The fact that the water content is so high suggests that the mechanical properties of the three hydrate structures should be similar to those of ice. This conclusion is true to a first approximation as shown in Table 2, with the exception of thermal conductivity and thermal expansivity (Davidson, 1983, Tse, 1994). Many mechanical properties of sH have not been measured to date.

Guest: Cavity Size Ratio: a Basis for Property Understanding. The hydrate cavity occupied is a function of the size ratio of the guest molecule within the cavity. To a first approximation, the concept of "a ball fitting within a ball" is a key to understanding many hydrate properties. Figure 2 (corrected from von Stackelberg, 1949) may be used to illustrate five points regarding the guest:cavity size ratio for hydrates formed of a single guest component in sI or sII.

1. The sizes of stabilizing guest molecules range between 0.35 and 0.75 nm. Below 0.35nm molecules will not stabilize sI and above 0.75 molecules will not stabilize sII.
2. Some molecules are too large to fit the smaller cavities of each structure (e.g. C_2H_6 fits in the $5^{12}6^2$ of sI; or $i\text{-C}_4\text{H}_{10}$ fits the $5^{12}6^4$ of sII).
3. Other molecules such as CH_4 and N_2 are small enough to enter both cavities (labeled as either $5^{12}+5^{12}6^2$ in sI or $5^{12}+5^{12}6^4$ in sII) when hydrate is formed of those single components.
4. The largest molecules of a gas mixture usually determines the structure formed. For example, because propane and *i*-butane are present in many thermogenic natural gases, they will cause sII to form. In such cases, methane will distribute in both cavities of sII and ethane will enter only the $5^{12}6^4$ cavity of sII.
5. Molecules which are very close to the hatched lines separating the cavity sizes appear to exhibit the most non-stoichiometry, due to their inability to fit securely within the cavity.

Table 3 shows the size ratio of several common gas molecules within each of the four cavities of sI and sII. Note that a size ratio (guest molecule: cavity) of approximately 0.9 is necessary for stability of a simple hydrate, given by the superscript "n". When the size ratio exceeds unity, the molecule will not fit within the cavity and the structure will not form. When the ratio is significantly less than 0.9 the molecule cannot lend significant stability to the cavity.

Consider ethane, which forms in the $5^{12}6^2$ cavity in sI, because ethane is too large for the small 5^{12} cavities in either structure and too small to give much stability to the large $5^{12}6^4$ cavity in sII. Similarly propane is too large to fit any cavity except the $5^{12}6^4$ cavity in sII, so that gases of pure propane form sII hydrates from free water. On the other hand, methane's size is sufficient to lend stability to the 5^{12} cavity in either sI or sII, with a preference for sI, because CH_4 lends slightly higher stability to the $5^{12}6^2$ cavity in sI than the $5^{12}6^4$ cavity in sII.

Phase Equilibrium Properties. In Figure 3 pressure is plotted against temperature with gas composition as a parameter, for methane+propane mixtures. Consider a gas of any given composition (marked 0 through 100% propane) on a line in Figure 3. At conditions to the right of the line, a gas of that composition will exist in equilibrium with liquid water. As the temperature is reduced (or as the pressure is increased) hydrates form from gas and liquid water at the line, so three phases (liquid water + hydrates + gas) will be in equilibrium. With further reduction of temperature (or increase in pressure) the fluid phase which is not in excess (gas in ocean environments) will be exhausted, so that to the left of the line the hydrate will exist with the excess phase (water).

All of the conditions given in Figure 3 are for temperatures above 273K and pressures along the lines vary exponentially with temperature. Put explicitly, hydrate stability at the three-phase (L-H-V) condition is always much more sensitive to temperature than to pressure. Figure 3 also illustrates the dramatic effect of gas composition on hydrate stability; as any amount of propane is added to methane the structure changes (sI \rightarrow sII) to a hydrate with much wider stability conditions. Note that a 50% decrease in pressure is needed to form sII hydrates, when as little as 1% propane is in the gas phase.

Any discussion of hydrate dissociation would be incomplete without indicating that hydrates provide the most industrially useful instance of statistical thermodynamics prediction of phase equilibria. The van der Waals and Platteeuw (1959) model was formulated after the determination of the crystal structures shown in Figure 1. With the model, one may predict the three-phase pressure or temperature of hydrate formation, by knowing the gas composition. For further discussion of these details the reader is referred to Sloan (1990, Chapter 5).

Heat of Dissociation. The heat of dissociation (ΔH_d) is defined as the enthalpy change to dissociate the hydrate phase to a vapor and aqueous liquid, with values given at temperatures just above the ice point. For sI and sII, Sloan and Fleyfel (1992) show that to a fair engineering approximation ($\pm 10\%$) ΔH_d is a function mostly of crystal hydrogen bonds, but also of the cavity occupied within a wide range of components sizes. Enthalpies of dissociation may be determined via the univariant slopes of phase equilibrium lines ($\ln P$ vs. $1/T$) in the previous paragraphs, using the Clausius-Clapeyron relation [$\Delta H_d = -zR d(\ln P)/d(1/T)$].

As one illustration, simple hydrates of C_3H_8 or $i\text{-C}_4\text{H}_{10}$ have similar ΔH_d of 129 and 133 kJ/mol (Handa, 1986) because the both occupy the $5^{12}6^4$ cavity, although their size:cavity ratios are somewhat different (0.943 and 0.976). As a second illustration, Figure 3 shows that mixtures of $\text{CH}_4 + \text{C}_3\text{H}_8$ have a value of $\Delta H_d = 79$ kJ/mol over a wide range of composition. In such mixtures, C_3H_8 occupies most of the $5^{12}6^4$ cavities while CH_4 occupies a small number of $5^{12}6^4$ and many 5^{12} . In fact, most natural gases (which form sII) have similar values of ΔH_d . Figure 4 shows similar line slopes (and thus ΔH_d values) for binary mixtures of methane when the large guest is changed from C_3H_8 , to $i\text{-C}_4\text{H}_{10}$, to $n\text{-C}_4\text{H}_{10}$. Similarly, over a wide range of composition for mixtures of methane and ethane, ΔH_d values are similar (74 kJ/mol) for components entering both cavities of sI. Identical arguments may be used to explain similar ΔH_d values of $79.5 \pm 7\%$ kJ/mol (Mehta and Sloan, 1996c) for sH mixtures of methane with seventeen larger components.

CHALLENGES FOR FUTURE RESEARCH

A review of the literature suggests that there are two imminent challenges for future research. First we must characterize the hydrate phase both in the laboratory and in the field. Secondly we must characterize the kinetics hydrates formation and dissociation.

Measurements of the Hydrate Phase. For the hydrate phase there are two measurement techniques - diffraction and spectroscopic. Neutron diffraction (typified by Tse, 1994) can detect water atoms and guest molecules, while X-ray diffraction detects oxygen positions. Recently using X-ray diffraction Stern et al. (1996) have been remarkably successful at converting 97% of ice to water, by raising ice grain temperatures above the solidus while under high pressure.

Two types of spectroscopy are useful with hydrates: (1) nuclear magnetic resonance (NMR) with cross polarization (CP) and magic-angle spinning (MAS), and (2) Raman spectroscopy. Virtually all NMR hydrate work to date comes from the Canadian National Research Council. The first comprehensive review of NMR studies of clathrates was written by Davidson and Ripmeester (1984), and a thorough update has been written by Ripmeester and Ratcliffe (1991). Of NMR hydrate compounds Xe has obtained prominence due to its large (ca. 100 ppm) chemical shift.

Recently Sum et al. (1996) have shown that Raman spectroscopy can be used to determine the fraction of filled cages in hydrates, and the fraction of various components in the cages. Since Raman appears to be both more versatile and less resource intensive, it holds substantial

Measurements of Hydrate Kinetics. Most hydrate kinetics research has come from the laboratory of Bishnoi, notably the work of Englezos et al., (1987a,b). They modeled kinetics of methane and ethane hydrate after nucleation, for periods up to 100 minutes. A subsequent model was made by Skovborg and Rasmussen (1994); these workers assumed that the mass transfer of gas to the liquid phase was the rate-controlling step, so that hydrate kinetics and diffusion to the hydrate phase could be ignored.

However, even with these excellent beginnings, quantification of hydrate kinetics still pose substantial challenges to hydrate researchers. For example, no model of hydrate nucleation can acceptably fit all the data of a single experimenter; no universal nucleation model is available. As another example, all models of hydrate growth kinetics are apparatus-dependent. While the growth model may be a satisfactory fit for the apparatus in which the data were generated, the model will not fit data generated in other apparatuses. Determining time-dependent hydrate behavior is one of the most significant challenges for research.

CONCLUSIONS

This tutorial reviews hydrate crystal structures, and shows how properties such as phase equilibria and heat of dissociation relate to molecular structure. While many time-independent properties of sI and sII hydrates are determined, those for newer structures (e.g. sH) are just beginning to be explored. The time-dependent characteristics of all three hydrate structures are largely unspecified and kinetic models to date appear to be apparatus-dependent. Characterization of the hydrate phase constitutes a current challenge.

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Table 1 Geometry of Cages in Three Hydrate Crystal Structures

Hydrate Crystal Structure	I		II		H		
Cavity	Small	Large	Small	Large	Small	Medium	Large
Description	5^{12}	$5^{12}6^2$	5^{12}	$5^{12}6^4$	5^{12}	$4^35^66^3$	$5^{12}6^8$
Number of Cavities/Unit Cell	2	6	16	8	3	2	1
Average Cavity Radius, Å	3.95	4.33	3.91	4.73	3.91 ¹	4.06 ³	5.71 ³
Variation in Radius, %	3.4	14.4	5.5	1.73	Not Available		
Coordination Number ²	20	24	20	28	20	20	36
Number of Waters/Unit Cell	46		136		34		

1. Variation in distance of oxygen atoms from center of cage.

2. Number of oxygens at the periphery of each cavity.

3. Estimates of structure H cavities from geometric models

Table 2 Comparison of Properties of Ice and sI and sII Hydrates¹

Property	Ice	Structure I	Structure II
<u>Spectroscopic</u>			
Crystallographic Unit Cell			
Space Group	P6 ₃ /mmc	Pm3n	Fd3m
No. H ₂ O molecules	4	46	136
Lattice Parameters at 273K	a =4.52 c =7.36	12.0	17.3
Dielectric Constant at 273 K	94	~58	58
Far infrared spectrum	Peak at 229 cm ⁻¹ .	Peak at 229 cm ⁻¹ with others	
H ₂ O Diffusion Correl Time, (μsec)	220	240	25
H ₂ O Diffusion Activ. Energy(kJ/m)	58.1	50	50
<u>Mechanical Property</u>			
Isothermal Young's modulus at 268 K (10 ⁹ Pa)	9.5	8.4 ^{est}	8.2 ^{est}
Poisson's Ratio	0.33	~0.33	~0.33
Bulk Modulus (272 K)	8.8	5.6	NA
Shear Modulus (272 K)	3.9	2.4	NA
VelocityRatio(Comp/Shear):272K	1.88	1.95	NA
<u>Thermodynamic Property</u>			
Linear. Therm. Expn: 200K (K ⁻¹)	56x10 ⁻⁶	77x10 ⁻⁶	52x10 ⁻⁶
AdiabBulkCompress:273K(10 ⁻¹¹ Pa)	12	14 ^{est}	14 ^{est}
Speed Long Sound:273K(km/sec)	3.8	3.3	3.6
<u>Transport</u>			
Thermal Conductivity:263K(W/m-K)	2.23	0.49±.02	0.51±.02

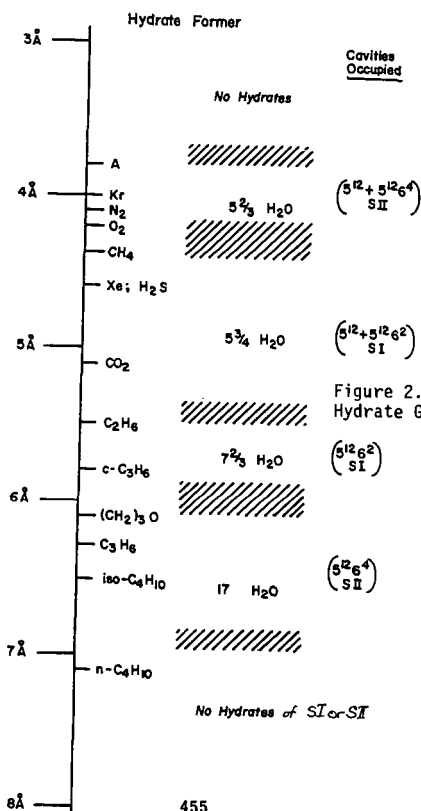
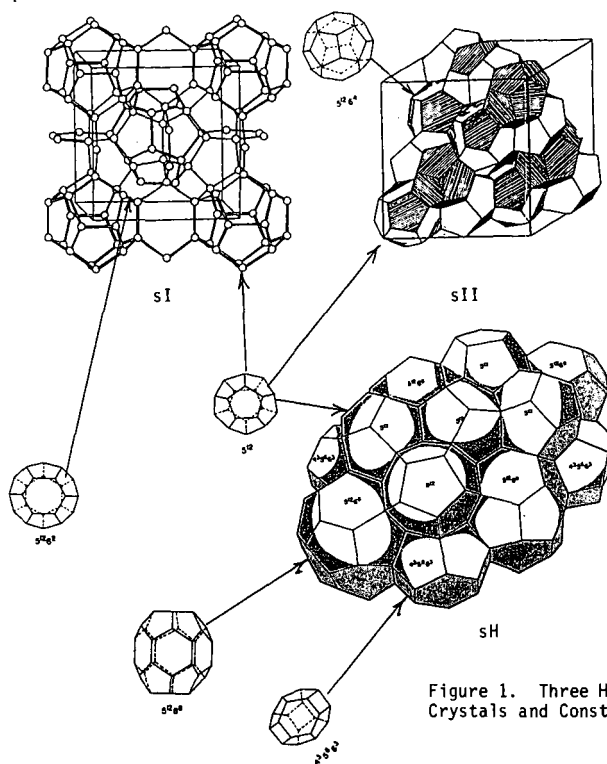
1. Modified from Davidson (1983) and from Ripmeester et al. (1994)

Table 3 Ratios of Molecular Diameters to Cavity Diameters¹ for Some Molecules Including Natural Gas Hydrate Formers

		(Molecular Diameter) / (Cavity Diameter)			
		Structure I		Structure II	
		5 ¹²	5 ¹² 6 ²	5 ¹²	5 ¹² 6 ⁴
Molecule	Guest Dmtr (Å)				
N ₂	4.1	0.804	0.700	0.817 [§]	0.616 [§]
CH ₄	4.36	0.855 [§]	0.744 [§]	0.868	0.655
H ₂ S	4.58	0.898 [§]	0.782 [§]	0.912	0.687
CO ₂	5.12	1.00	0.834 [§]	1.02	0.769
C ₂ H ₆	5.5	1.08	0.939 [§]	1.10	0.826
C ₃ H ₈	6.28	1.23	1.07	1.25	0.943 [§]
i-C ₄ H ₁₀	6.5	1.27	1.11	1.29	0.976 [§]
n-C ₄ H ₁₀	7.1	1.39	1.21	1.41	1.07

[§] indicates the cavity occupied by the simple hydrate former

1. cavity radii from Table 2-1 minus 1.4Å water radii



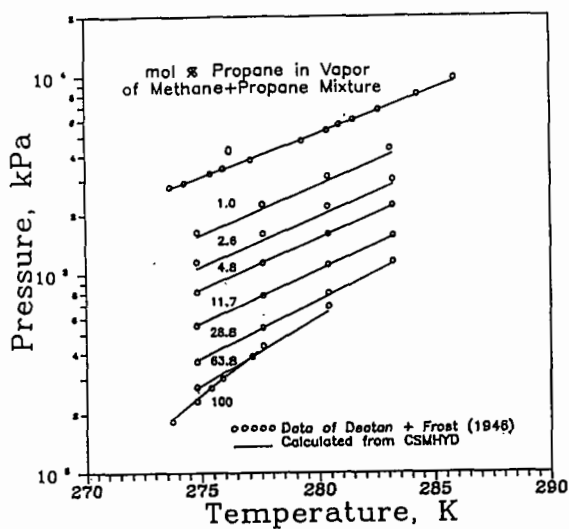


Figure 3. Three-Phase (Lw-H-V) Equilibria of Methane+Propane Mixtures

Figure 4. Three-Phase Equilibria of Methane +(Propane and Two Butanes)

